CLAIMS

What is claimed is:

1. A method for recovering and producing C_4-C_6 dicarboxylates from an alkaline waste solution generated in a caprolactam preparation process, comprising the steps of:

(1) neutralizing the alkaline waste solution generated from the caprolactam preparation process and adjusting a pH value thereof with sulfuric acid to separate into an aqueous phase and an organic phase; adding nitric acid to the organic phase for oxidizing and converting valuable substances contained in the organic phase into dicarboxylic acids, thereby obtaining an oxidized reaction mixture containing dicarboxylic acids;

(2) introducing the oxidized reaction mixture obtained from the step (1) into a two-stage concentration apparatus; in first-stage concentration, distilling out low boiling-point monocarboxylic acids and nitric acid; in second-stage concentration, decomposing remaining nitric acid and nitrocompounds, so as to obtain crude concentrates mainly containing C_4-C_6 dicarboxylic acids;

(3) adding C_1-C_4 alkyl alcohol to the crude concentrates mainly containing C_4-C_6 dicarboxylic acids obtained from the step (2), and proceeding two-stage esterification, whereby half-esterified intermediates are obtained in first-stage esterification, and crude dicarboxylates are obtained in second-stage esterification; and

(4) distilling the crude dicarboxylates obtained from the step (3), so as to get single-species dicarboxylates or a mixture of dicarboxylates.

2. The method of claim 1, wherein in the step (1), at least one oxidant other than nitric acid is added to the organic phase.

3. The method of claim 2, wherein the oxidant is selected a group consisting of hydrogen peroxide, perchloric acid and potassium permanganate.
4. The method of claim 1, wherein concentration of nitric acid is 10 to 90%.
5. The method of claim 1, wherein a weight ratio of nitric acid to the organic phase is 0.5 to 30:1.
6. The method of claim 2, wherein the oxidant is added in a ratio of 0 to 5%.
7. The method of claim 1, wherein oxidation and conversion of the step (1) are performed under conditions including: at least one reaction stage, reaction temperature of a range from 10 to 150°C, and reaction mixture flowing from first to last reaction stage with the reaction temperature being increased gradually at stage intervals of 5 to 30°C, reaction time for each stage being set as 5 minutes to 4 hours, and reaction pressure being absolute pressure 0.5 to 2kg/cm^2.
8. The method of claim 1, wherein in the step (2), the first-stage concentration is performed at temperature of 50 to 120°C and absolute pressure of 0.2 to 1.5 kg/cm^2, the second-stage concentration is carried out at temperature of 120 to 200°C and absolute pressure of 0.5 to 2.0 kg/cm^2.
9. The method of claim 1, wherein the C_1-C_4 alkyl alcohol used in the step (3) is selected from a group consisting of methanol, ethanol, propanol and butanol.
10. The method of claim 1, wherein a weight ratio of the C_1-C_4 alkyl alcohol to the crude concentrates of dicarboxylic acids is 1-15:1.
11. The method of claim 9, wherein a weight ratio of the C_1-C_4 alkyl alcohol to the crude concentrates of dicarboxylic acids is 1-15:1.

12. The method of claim 1, wherein a catalyst is added in the step (3), and selected from a group consisting of sulfuric acid, phosphoric acid, nitric acid, alkanesulfonic acids, benzenesulfonic acid and cation exchange resin.

13. The method of claim 12, wherein the catalyst is added in an amount of 0 to 5%.

14. The method of claim 1, wherein in the step (3), the first-stage esterification is performed at temperature of 40 to 120°C, absolute pressure of 0.2 to 1.2 kg/cm^2, and esterification time of 0.5 to 8 hours; and the second-stage esterification is carried out at temperature of 80 to 200°C, absolute pressure of 0.8 to 2.5 kg/cm^2, and esterification time of 0.5 to 8 hours.

15. The method of claim 1, wherein a distillation apparatus used in the step (4) is of tray or packing type.

16. The method of claim 14, wherein distillation of the step (4) is performed by using 10 to 100 trays theoretically, and under absolute pressure of 0.02 to 1.0 kg/cm^2 and temperature of 70 to 250°C.

17. The method of claim 1, comprising the steps of:

(1) neutralizing the alkaline waste solution generated from the caprolactam preparation process and adjusting a pH value thereof with sulfuric acid to separate into an aqueous phase and an organic phase; adding nitric acid of 10 to 90% concentration to the organic phase in a weight ratio of nitric acid to the organic phase at 0.5 to 30:1, and oxidizing and converting valuable substances contained in the organic phase into dicarboxylic acids, thereby obtaining an oxidized reaction mixture containing dicarboxylic acids;

(2) introducing the oxidized reaction mixture obtained from the step (1) into a two-stage concentration apparatus, wherein first-stage concentration is

performed at temperature of 50 to 120°C and absolute pressure of 0.2 to 1.5 kg/cm^2, and second-stage concentration is carried out at temperature of 120 to 200°C and absolute pressure of 0.5 to 2.0 kg/cm^2, so as to obtain crude concentrates mainly containing C_4-C_6 dicarboxylic acids;

(3) adding C_1-C_4 alkyl alcohol to the crude concentrates mainly containing C_4-C_6 dicarboxylic acids obtained from the step (2), and proceeding two-stage esterification, wherein first-stage esterification is performed at temperature of 40 to 120°C, absolute pressure of 0.2 to 1.2 kg/cm^2, and esterification time of 0.5 to 8 hours; and second-stage esterification is carried out at temperature of 80 to 200°C, absolute pressure of 0.8 to 2.5 kg/cm^2, and esterification time of 0.5 to 8 hours, so as to obtain crude dicarboxylates; and

(4) introducing the crude dicarboxylates obtained from the step (3) into a tray- or packing-type distillation tower for performing distillation by using 10 to 100 trays theoretically, and under absolute pressure of 0.02 to 1.0 kg/cm^2 and temperature of 70 to 250°C, so as to get single-species dicarboxylates or a mixture of dicarboxylates.